Symmetric Diblock Copolymer Thin Films Confined Between Two Hard Surfaces: Simulations and Theory

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Diblock copolymers in the bulk are known to exhibit a variety of mesoscale ordered structures, including spheres, cylinders and lamellae. In some applications of nano-fabrication (e.g., nanolithography), long-range ordered lamellae perpendicular to a substrate are desirable, which could be obtained by depositing symmetric diblock copolymers on nano-patterned chemically heterogeneous surfaces. In this work, the morphology of thin films of symmetric diblock copolymers confined between two hard and flat surfaces was explored by means of Monte Carlo simulations in the framework of a simple cubic lattice model. For such simulations, the match between the bulk lamellar period and the simulation box size is crucial to obtain meaningful results. The simulations were performed in an expanded grand-canonical ensemble, where the chemical potential and the temperature of the confined film were specified and its density was allowed to fluctuate. We have investigated systematically the thin films confined between two homogeneous surfaces and between patterned-homogeneous surfaces. Our simulations have revealed various types of morphology, depending on the surface configurations.

To construct the phase diagram for confined thin films, we have combined the results of simulations with a phenomenological theory. The simulations provide valuable insights into the lowest free-energy morphologies that are required by the theory; these structures are sometimes difficult to guess by simple intuition. The theory is useful for rationalizing the simulation results and for designing experimental protocols that will permit long-range patterning of nanoscale features. Two conditions are found to be essential for obtaining long-range ordered perpendicular lamellae: a lower stripe-patterned surface with pattern period comparable to the bulk lamellar period, and an upper neutral or weakly preferential surface. These conditions are confirmed experimentally.